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Structure, ferroelectric and local piezoelectric properties of KNN- based perovskite ceramics

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Lead-free ferroelectric materials continue to be intensively studied in order to replace widely used lead-based ones [1-4]. We studied influence of cation substitutions and preparation conditions on structure, microstructure, ferroelectric, and local piezoelectric properties of solid solutions in the systems on the base of sodium-potassium niobate $(K_{0.5}Na_{0.5})NbO_3$ (KNN) with perovskite structure [5-7].

Ceramic samples in the KNN-based systems were prepared by the two-step solid-state reaction method at temperatures of 900-1500 K. Solid solutions with Ba^{2+}, Li^{+}, Ca^{+} in A- and with Cu^{2+}, Mn^{3+}, Ni^{2+}, Fe^{3+} cations in B-sites of perovskite lattice were prepared. To improve density of ceramics overstoichiometric additives (KCl, LiF and ZnO) were used.

To characterize the samples, complex of physico-chemical methods was used: the X-ray Diffraction, Scanning Electron Microscopy (SEM), Second Harmonic Generation (SHG), Dielectric Spectroscopy (DS), and Atomic Force Microscopy in Piezoresponse Force Mode (PFM) methods.

The observed unit cell volume changes in modified KNN-based ceramics depended on ionic radii of substituting cations. Mean size of grains changed from ~3 till ~20 μm in compositions containing low melting additives KCl and LiF. Ferroelectric phase transitions at ~400 and near 700 K were confirmed using the DS and SHG methods. At temperatures higher than ~900 K effects of dielectric relaxation caused by formation of oxygen vacancies were observed in ceramics with aliovalent substitutions.

Increase in the spontaneous polarization value while non monotonous changes in dielectric permittivity values and were revealed for modified ceramics at the room temperature. Ferroelectric polarization switching at nanoscale was observed using PFM method, and in KNN-based ceramics high values of effective d_{33} piezoelectric coefficient 200-300 pm/V reached. The results obtained confirm the statement of prospects of creating new lead-free materials on the base of modified KNN- based compositions.

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